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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/EP98/04001 <b>(22) International Filing Date:</b> 17 June 1998 (17.06.98)  <b>(30) Priority Data:</b> 9/165648 23 June 1997 (23.06.97) JP  <b>(71) Applicant (for all designated States except US):</b> ELF ATOCHEM S.A. [FR/FR]; 4/8, cours Michelet, F-92800 Puteaux (FR).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> MIYAKI, Yoshiyuku [JP/JP]; Elf Atochem Japan K.K., Kyoto Technical Center, 1, Chudoji, Awata-cho, Chudoji, Shimogyo-ku, Kyoto 600 (JP). OHASHI, Kazuyoshi [JP/JP]; Elf Atochem Japan K.K., Kyoto Technical Center, 1, Chudoji, Awata-cho, Chudoji, Shimogyo-ku, Kyoto 600 (JP).  <b>(74) Agent:</b> KAPLAN, Jean-Pierre; Elf Atochem S.A., 4/8, cours Michelet, La Défense 10, F-92091 Paris La Défense Cedex (FR).		<b>(81) Designated States:</b> CA, CN, JP, KR, SG, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> A BATTERY SEPARATOR, ITS METHOD OF PRODUCTION AND ANON-AQUEOUS SECONDARY BATTERY		
<b>(57) Abstract</b>  [Objective]: the objective of the present invention lies in offering a battery separator comprising a polyvinylidene fluoride resin porous body which is outstanding in its mechanical strength and ionic conductivity, and a method of producing a lithium secondary battery or other such non-aqueous secondary battery which is thin and outstanding in its flexibility and mechanical strength. [Constitution]: a battery separator characterized in that it comprises a polyvinylidene fluoride resin porous body, in which porous body is dispersed inorganic filler, a method for the production thereof; and a non-aqueous secondary battery where, in a non-aqueous secondary battery constructed from a negative electrode, positive electrode and separator, the separator is constructed of said polyvinylidene fluoride resin porous body.		

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**A battery separator, its method of production and a non-aqueous secondary battery**

[Industrial Field of Utilization]

5 The present invention relates to a battery separator, its method of production and a non-aqueous secondary battery employing this separator. The objective thereof lies in offering a method for producing a non-aqueous secondary battery such as a lithium secondary battery which is thin and outstanding in its flexibility and mechanical strength.

[Prior-Art]

The separator employed in a lithium battery or other such non-aqueous battery has the role of preventing short-circuiting between the positive and negative electrodes, and of ensuring electroconductivity by the retention of electrolyte in the numerous pores introduced in the separator. Hitherto, typical separators have been polyethylene (PE) and polypropylene (PP) porous membranes, two-layer membranes in which PE and PP are affixed together, and three-layer membranes in which PE is sandwiched between PP, etc. However, PE and PP are flammable materials and, in lithium batteries in particular, there is a desire for a more highly safe material.

25 Recently, there has been proposed a lithium battery which employs, as the separator (macromolecular gel electrolyte), a vinylidene fluoride copolymer film which has been swollen by a solution formed by dissolving  $\text{LiPF}_6$  or other such Li salt in a carbonate solvent [JP Kokai 8-507407 and 8-509100]. In the construction of such a battery, a film comprising vinylidene fluoride copolymer and plasticizer is produced, after which a complex stage is needed involving either removal of the plasticizer from the film using a low-boiling solvent or replacement with an electrolyte solution. Moreover, the vinylidene fluoride copolymer film swollen with the solvent normally has inadequate temperature resistance at high temperatures (50°C and

above), whereas at low temperatures (0°C and below) the battery properties, such as capacity, tend to be reduced. Again, there has been proposed the use of a porous film comprising polyvinylidene fluoride resin as the separator  
5 (Japanese Unexamined Patent Publication No. 8-250127; Toriyama et al, Abstracts of the 37th Symposium on Batteries [Dai 37-kai Denchi Toronkai Koen Yoshishu], page 239, 1996). According to these references, the polyvinylidene fluoride resin is swollen (plasticized) by  
10 means of an organic electrolyte liquid, and since the matrix region thereof also contributes to the ionic conductivity, when this porous film is employed as a separator, a greater ionic conductivity is obtained than when a polyethylene or polypropylene porous film is used.  
15 However, in such circumstances, a porous film with a high level of porosity is required for obtaining high ionic conductivity, and so the mechanical strength of the separator becomes a problem.

[Problem to be Resolved by the Invention]

20 As a result of investigations to resolve the problems of conventional polyethylene and polypropylene porous bodies, and of macromolecular gel electrolytes, and to obtain a polyvinylidene fluoride resin porous body which is outstanding in its mechanical strength and ionic  
25 conductivity, the present inventors have arrived at the present invention.

[Means for Resolving the Problem]

The present invention relates to a battery separator which is characterized in that it comprises a poly-vinylidene  
30 fluoride resin porous body, and an inorganic filler is dispersed in said porous body.

The "polyvinylidene fluoride resin" employed in the present invention is a thermoplastic fluoro-resin containing at least 50 wt%, and preferably at least 75 wt%, of vinylidene  
35 ~~fluoride as resin structural units.~~ Consequently, it is not restricted to homopolymer comprising vinylidene-fluoride alone, and it may also be a copolymer of

vinylidene fluoride and one or more than one type of monomer selected from the following monomers. As examples of copolymerizable monomers there are tetra-fluoroethylene, trifluoroethylene, trifluorochloro-ethylene, vinyl chloride, hexafluoropropylene, ethylene and perfluoroalkyl vinyl ether, etc. As the polyvinylidene fluoride copolymer, there is preferably used a copolymer of vinylidene fluoride and hexafluoro-propylene (of hexafluoropropylene content no more than 15 wt%). Such thermoplastic polyvinylidene fluoride resins can be obtained by emulsion polymerization, suspension polymerization and other such generally-employed polymerization methods, and the melt flow rate (MFR) value will preferably be from 0.005 to 100 g/10 min (measured at 230°C under a 2.16 kg load) and more preferably from 0.01 to 20 g/10 min.

In the present invention, per 100 parts by weight of the polyvinylidene fluoride resin, there is included from 2 to 200 parts by weight, and more preferably from 5 to 50 parts by weight, of inorganic filler.

As the inorganic filler used in the present invention, it is possible to employ the many types generally used in high polymer materials (see "The Dictionary of Filler Application [Fira Katsuyo Jiten]", edited by the Fira Kenkyukai, published by Taiseisha, 1994). In particular, inorganic oxides and silicates are preferably employed. As examples of the inorganic oxides, there are silica, alumina, diatomaceous earth, titanium oxide, calcium oxide, zinc oxide, magnesium oxide, tin oxide, ferrite and the like. Of these, the use of alumina and of silica produced by a decomposition method is especially preferred. Further, as examples of silicates, there are calcium silicate, talc, mica, montmorillonite, bentonite, sepiolite, imogolite, sericite, glass fibre and glass beads, etc. The shape of the inorganic filler is not particularly restricted, and it can be fibrous, needle-shaped, platelet-shaped or granular.

Further, the surface of the aforesaid inorganic filler can be rendered hydrophobic by the reaction of the functional groups having hydroxyl groups present at the surface, such as silanol groups, with a silane compound such as a halosilane, alkoxysilane, silazane, siloxane or the like.

The method of producing the battery separator of the present invention is not particularly restricted, and it is possible to employ the known methods for producing porous bodies from high polymer resins. As a typical method, there is the method known as the sol-gel method which uses a solution of the high polymer resin and a non-solvent. Specifically, the aforesaid inorganic filler is dispersed in a solution obtained by dissolving the polyvinylidene fluoride resin in a solvent, and then a porous body is obtained by bringing this solution into contact with a non-solvent for the polyvinylidene fluoride resin. In such circumstances, as solvents for dissolving the polyvinylidene fluoride resin, there are N-methylpyrrolidone, formamide, dimethylformamide, dimethylacetamide, dimethylsulphoxide,  $\gamma$ -butyrolactone, tetramethylurea, trimethyl phosphate, acetone, methyl ethyl ketone, tetrahydrofuran and the like. Moreover, mixtures of these may also be used as the solvent. The concentration of polyvinylidene fluoride resin contained in the solution is normally from 5 to 50 wt%, and preferably from 10 to 30 wt%. As the poor solvent, water or alcohols are preferably employed, with water being especially preferred.

By bringing the solution of the poly-vinylidene fluoride resin containing dispersed inorganic filler, prepared as described above, into contact with a poor solvent, the sol-gel transformation is immediately initiated and a porous body produced. In such circumstances, it is preferred that contact be effected with the poor solvent for a sufficiently long time to extract the solvent from within the porous body, using a poor solvent with a low content of solvent for dissolving the polyvinylidene fluoride resin.

This contacting time will vary according to the size of the porous body but, normally, at least 10 seconds is preferred, and more preferably at least 30 seconds.

The desired porous body shape for a battery separator is that of a film. The thickness is preferably from 5 to 200  $\mu\text{m}$ , more preferably from 10 to 100  $\mu\text{m}$ . The pore diameter is preferably no more than 20  $\mu\text{m}$ , and more preferably from 0.05 to 10  $\mu\text{m}$ . In terms of the porosity, from 5 to 85% is preferred, with from 20 to 80% further preferred.

The porous body of the present invention may also, where required, be drawn (hot drawn or cold drawn) or subjected to some treatment, or both, to raise the degree of crystallization or to fix the crystal structure. The draw ratio will vary according to the type of resin (molecular weight and co-monomer content) and the porous body production conditions, etc, but will appropriately be from 1.1 to 6, but less than the draw ratio at break, and preferably from 1.2 to 4. The drawing may be uniaxial or biaxial (simultaneous or consecutive). The recommended heat-treatment temperature is from 70 to 155°C, and preferably 100 to 150°C. Heat treatment may be performed in the free state, or under controlled shrinkage, at a fixed length or in a stretched state, but where a stretched state is employed the percentage stretch will ideally be no more than 10%, and preferably no more than 5%. In short, it is preferred that this be within a range such that spherulites formed at the time of the melt solidification are not broken down, and growth occurs in the state prior to breakdown and transformation to fine crystals.

It is possible to introduce crosslinks into the porous body of the present invention by exposure to a high energy (normally from 2 to 40 megarad) electron beam or to  $\gamma$ -rays, or by a chemical dehydrofluorination reaction. In this way, it is possible to enhance the heat resistance or mechanical strength of the porous body.

Below, the application of a porous film obtained in the manner described above to a lithium battery is explained.



Specifically, using an anode produced by forming a layer of anode active material on at least one face of a current collector, a cathode produced by forming a layer of cathode active material on at least one face of a current collector, and the aforesaid porous film, this porous film is interposed between the anode and cathode such that they do not touch, and these are either laminated or wound in the form of a roll (a spiral shape) and then accommodated in a suitable container. To this is added an electrolyte solution formed by dissolving at least one type of lithium salt selected from  $\text{LiPF}_6$ ,  $\text{LiBF}_4$ ,  $\text{LiClO}_4$ ,  $\text{LiAsF}_6$ ,  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ ,  $\text{LiCF}_3\text{SO}_3$  and  $\text{LiSbF}_6$ , etc, in a suitable solvent (chiefly a carbonate such as ethylene carbonate, propylene carbonate or dimethyl carbonate, etc), and the container then sealed to finally obtain the battery. In other words, the porous film of the present invention is employed in a state such that the porous regions are filled with the aforesaid electrolyte solution and, at the same time, the matrix region of the porous film, which comprises polyvinylidene fluoride resin, is in a state swollen by the electrolyte solution.

Here, as the current collector in the electrodes, there may be used a metal foil, metal mesh or three-dimensional porous body, etc, but it is preferred that the metal employed in the current collector be a metal which cannot readily alloy with lithium. In particular, iron, nickel, cobalt, copper, aluminium, titanium, vanadium, chromium and manganese can be employed, on their own or as alloys thereof.

Of the electrode active materials, the negative electrode active material should be a material which can undergo doping and undoping with lithium ions. Examples of such materials are coke materials like petroleum-based or carbon-based coke, etc, acetylene black or other such carbon black, graphite, glassy carbon, active carbon, carbon fibre and carbonaceous materials such as fired organic polymers obtained by the firing of organic high

polymers in a non-oxidizing atmosphere. Moreover, copper oxide may also be added.

As the positive electrode active material, there can be used transition metal oxides such as manganese oxides and vanadium pentoxide, transition metal oxides such as iron oxide and titanium oxide, and composite compounds of these with lithium (e.g. lithium cobalt composite oxide, lithium cobalt nickel composite oxide and lithium manganese oxide) and the like. When incorporating such a material into a positive electrode, a solvent is mixed with the mixture obtained by adding suitable amounts of electro-conductor (carbon is most often used) and binder to the powder-form positive electrode active material, to produce a paste, which is then applied to the current collector and dried, after which pressing is optionally carried out and the electrode obtained.

[Examples]

Below, the present invention is explained in more specific terms by means of some examples but the invention is not to be restricted merely to these.

[Example 1]

15 parts by weight of Kynar 741 (polyvinylidene fluoride resin made by Elf Atochem; MFR value 0.3 g/10 min [measured at 230°C under a 2.16 kg load]) was dissolved in 85 parts by weight of N-methylpyrrolidone. In this solution was dispersed 4 parts by weight of non-crystalline silica (primary particle size 20 nm) obtained by a pyrolysis method from silicon tetrachloride and hydrogen, after which the mixture was cast onto a polyethylene terephthalate supporting film and immersed for 2 hours in water, and a porous film of thickness 50  $\mu\text{m}$  obtained. The silica content of this film was 21 wt%. The film had a porosity of about 40% and numerous approximately 1  $\mu\text{m}$  pores were noted in the interior.

~~This film was immersed for 1 hour in an electrolyte solution obtained by dissolving a concentration of 1M  $\text{LiPF}_6$  in a 1 : 1 mixture of ethylene carbonate (EC) and propylene~~

carbonate (PC), after which its conductivity was measured using an ordinary bridge. A value about three times that of Comparative Example 1 was obtained. When this film which had been swollen with electrolyte solution was heated to 60°C, it was found that the film shape was stable and did not break down.

[Example 2]

Using, as a negative electrode active material support, coal pitch coke which had been subjected to grinding in a ball mill, 100 parts by weight thereof was added to a solution formed by dissolving 10 parts by weight of polyvinylidene fluoride (Kynar 301F made by Elf Atochem; MFR 0.03 g/10 min at 230°C under a 2.16 kg load) as a binding agent in N-methylpyrrolidone, and a slurry (paste) formed. This slurry was applied to both sides of copper foil of thickness 20 µm and, after leaving for 1 hour at 120°C, reduced-pressure drying and pressing were performed and a negative electrode of thickness 140 µm and width 20 mm was obtained.

Next, a positive electrode was obtained in the following manner. 100 parts by weight of LiCoO<sub>2</sub> as the positive electrode active material, and 6 parts by weight of graphite as an electro-conductive agent, were dispersed in N-methylpyrrolidone with 10 parts by weight of polyvinylidene fluoride (Kynar 301F) as a binding agent, to produce a slurry (paste). This slurry was applied to both faces of aluminium foil of thickness 20 µm and, after leaving for 1 hour at 120°C, reduced-pressure drying and pressing were performed and a positive electrode of thickness 160 µm and width 20 mm was obtained.

Using the negative and positive electrodes thus obtained, together with the porous film obtained in Example 1 as a separator, these were respectively superimposed in the order separator, negative electrode, separator, positive electrode and separator, after which the laminate was rolled in the form of a spiral and a spiral-shaped electrode body obtained. Next, after connecting lead wires

to the respective electrodes in this electrode body, it was introduced into a stainless steel container, into which was poured, as the electrolyte, a solution of 1 M  $\text{LiPF}_6$  dissolved in an equal volume mixture of propylene carbonate and 1,2-dimethoxyethane.

In a charging/discharging test, charging was carried out initially to 4.1 V at a current density of 30 mA per 1 g of carbon and then, in the same way, discharging was carried out to 2.5 V at the same current. The second time, and thereafter, charging and discharging were repeated under the same conditions and an evaluation of the battery carried out based on the discharge capacity. As a result, the discharge capacity in the 100th cycle was excellent, being at least 60% that in the 10th cycle.

[Example 3]

A porous film was prepared in the same way as in Example 1 excepting that, instead of the Kynar 741, there was used Kynar 2801 which is a copolymer of vinylidene fluoride and hexafluoropropylene made by Elf Atochem (hexafluoropropylene content about 10 wt%, MFR value 0.2 g/10 min [measured at 230°C under a 2.16 kg load]) and, instead of the silica, there was used fine particles of  $\alpha$ -alumina. The alumina content in this film was 21 wt%. The film had a porosity of about 30% and numerous approximately 1  $\mu\text{m}$  pores were noted in the interior. Further, when the electro-conductivity was measured in the same way as in Example 1, a value about three times that of Comparative Example 2 was obtained.

[Comparative Example 1]

A solution obtained by dissolving 15 parts by weight of Kynar 741 in 85 parts by weight of N-methylpyrrolidone was cast on a polyethylene terephthalate supporting film, then immersed for 2 hours in water and a porous film of thickness 50  $\mu\text{m}$  obtained. This film had a porosity of about 40% and numerous approximately 1  $\mu\text{m}$  pores were noted in the interior.

The film was immersed for 1 hour in an electrolyte solution obtained by dissolving a concentration of 1M  $\text{LiPF}_6$  in a 1 : 1 mixture of ethylene carbonate (EC) and propylene carbonate (PC). Subsequently, when its conductivity was measured using an ordinary bridge, it was found to be 0.3 mS/cm.

[Comparative Example 2]

A porous film was prepared in the same way as in Comparative Example 1 excepting that, instead of the Kynar 741 in Comparative Example 1, there was used Kynar 2801. The film had a porosity of about 30% and numerous approximately 1  $\mu\text{m}$  pores were noted in the interior. Further, when the conductivity was measured in the same way as in Comparative Example 1, it was 0.4 mS/cm.

[Effects of the Invention]

As explained above, the battery separator of the present invention possesses high ionic conductivity, its production is easy and it has outstanding mechanical characteristics. When it is employed as a lithium battery separator, since the polyvinylidene fluoride resin is flame-retardant, there is formed a battery which is much safer than when a polyethylene separator is used.

## Claims

1. A battery separator which is characterized in that it comprises a polyvinylidene fluoride resin porous body, and an inorganic filler is dispersed in said porous body.

5        2. A battery separator according to Claim 1 where the polyvinylidene fluoride resin is vinylidene fluoride homopolymer.

3. A battery separator according to Claim 1 where the polyvinylidene fluoride resin is a copolymer of vinylidene  
10 fluoride and at least one monomer selected from tetrafluoroethylene, hexafluoropropylene, trifluoroethylene and trifluorochloroethylene, and the proportion of the vinylidene fluoride component in said copolymer is at least 50 wt%.

15        4. A battery separator according to Claims 1 to 3 where there is included from 2 to 200 parts by weight of the inorganic filler per 100 parts by weight of the polyvinylidene fluoride resin.

5. A battery separator according to Claims 1 to 4  
20 where the inorganic filler is selected from inorganic oxides and silicates.

6. A battery separator according to Claim 5 where at least one type of inorganic filler is included selected from types of silica and alumina.

25        7. A battery separator according to Claim 1 produced by dissolving polyvinylidene fluoride resin in a solvent to form a solution, in which is dispersed the inorganic filler, and then this solution is brought into contact with a polyvinylidene fluoride resin non-solvent.

30        8. A method of producing a battery separator comprising a polyvinylidene fluoride resin porous body, by dissolving polyvinylidene fluoride resin in a solvent to form a solution, in which is dispersed an inorganic filler, and then this solution is brought into contact with a  
35 ~~polyvinylidene fluoride resin non-solvent.~~

9. A non-aqueous secondary battery which is characterized in that, in a non-aqueous secondary battery

comprising positive electrode, separator and negative electrode, the separator comprises a polyvinylidene fluoride resin porous body in which inorganic filler has been dispersed.

5        10. A non-aqueous secondary battery according to Claim 9 where the polyvinylidene fluoride resin porous body comprises polyvinylidene fluoride homopolymer.

10        11. A non-aqueous secondary battery according to Claim 9 where the polyvinylidene fluoride resin porous body comprises a copolymer which is a copolymer of vinylidene fluoride and at least one monomer selected from tetrafluoroethylene, hexafluoropropylene, trifluoroethylene and trifluorochloroethylene, and the proportion of the vinylidene fluoride component in said copolymer is at  
15        least 50 wt%.

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# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/EP 98/04001

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 H01M2/16

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	US 5 429 891 A (GOZDZ ANTONI S ET AL) 4 July 1995 see column 4, line 64 - column 5, line 9 see column 5, line 35 - line 40 see column 6, line 45 - line 50 see column 7, line 25 - line 30 ---	1, 3-9, 11
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☒ Further documents are listed in the continuation of box C.

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International Application No  
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Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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